

Quantum mechanical ab-initio simulation of the electron screening effect in metal deuteride crystals

A. Huke¹, K. Czerski^{1,2}, S. M. Chun^{1a}, A. Biller¹, and P. Heide¹

¹ Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

² Institute of Physics, University of Szczecin, Szczecin, Poland

Abstract. In antecedent experiments the electron screening energies of the d+d reactions in metallic environments have been determined to be enhanced by an order of magnitude in comparison to the case of gaseous deuterium targets. The analytical models describing averaged material properties have not been able to explain the experimental results so far. Therefore, a first effort has been undertaken to simulate the dynamics of reacting deuterons in a metallic lattice by means of an ab-initio Hartree-Fock calculation of the total electrostatic force between the lattice and the successively approaching deuterons via path integration. The calculations have been performed for Li and Ta, clearly showing a migration of electrons from host metallic to the deuterium atoms. However, in order to avoid more of the necessary simplifications in the model the utilization of a massive parallel supercomputer would be required.

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1 Introduction

Following our first observation [1,2,3] of the grossly enhanced screening effect for the d+d reactions in metals resulting in an exponential-like increase of the astrophysical S-factors towards lower energies other groups reproduced our results [4,5,6,7,8,9]. The measured screening energies are one order of magnitude larger than for D₂-gas targets [10]. However, particular care is required for the interpretation of the experimental data because the special physico-chemical properties of the hydrogen compounds and the beam induced chemical reactions at the target heavily influence the obtained screening energy results [3, 11]. Originally, the screening energy was extracted using the simple model of [12] treating it as an shift of the kinetic energy. Thus, the screening energy is merely a parameter which describes the modification of the Coulomb barrier and not a real energy gain for the projectile. In a microscopic view it is universally valid that the screening effect depends on the impact of the electronic configuration of the environment on the Coulomb barrier of the entrance channel only, i.e. the pure Coulomb energy is simply modified by a Yukawa factor $W(r) = \frac{1}{4\pi\epsilon_0} \frac{Z_p Z_t e^2}{r} e^{-\frac{r}{\lambda_A}}$ with λ_A being the screening length. As such the inferred screening energy is merely the second term in a Taylor-expansion

of $W(r)$, i.e. $U_e = \frac{1}{4\pi\epsilon_0} \frac{Z_p Z_t e^2}{\lambda_A}$, and a coarse mathematical parametrization in the simple model.

The experimental screening energy values could not be described by theoretical approaches to this extent. In [13,14] we presented an analytical model based on the dielectric function theory for the description of the screening effect. Its results, however, are below the measured screening energies by a factor of 2 though better than other approaches cited therein, e.g. [15]¹. Therefore, a first effort was undertaken to simulate the pre-reaction impact with an ab-initio quantum mechanical Hartree-Fock calculation which is able to consider the actual crystal structure while the analytical model only operates on averaged material properties. The concrete form of the electron density distribution around the nucleus indeed influences the screening energy to a great extent as was shown in [17] on a D₂ molecule with a time dependent Hartree-Fock calculation. Due to the many electrons involved in the simulation of the crystal the time dependency can not be retained on a workstation class computer. The model is described in the next section permitting the assessment of the necessary simplifications.

^a deceased

Correspondence to: huke@physik.TU-Berlin.DE, Armin.Huke@web.de

¹ The Debye-Hückel model proposed in [8] is utterly inapplicable for the frozen electron gas in condensed matter [14, 16].

2 Mathematical Model

The mathematical model, the simulation is based on, results from a hierarchy of simplifications in the theoretical description of the physical reality leading to more or less severe deviations in the obtained values of the observables.

The originator for it is the non-relativistic spin independent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi = \mathbf{H} \Psi \quad (1)$$

with the Hamilton operator for the crystal molecule

$$\mathbf{H} = - \sum_a^K \frac{\hbar^2}{2M_a} \Delta_a + \frac{e^2}{4\pi\epsilon_0} \sum_{a<b}^K \frac{Z_a Z_b}{R_{ab}} \quad (2)$$

$$- \sum_i^N \frac{\hbar^2}{2m_e} \Delta_i - \frac{e^2}{4\pi\epsilon_0} \sum_i^N \sum_a^K \frac{Z_a}{r_{ai}} \quad (3)$$

$$+ \frac{e^2}{4\pi\epsilon_0} \sum_{i<j}^N \frac{1}{r_{ij}} \quad (4)$$

containing both kinetic and potential operators for the K nuclei (2) and the N electrons (3, 4)². Therein Z_a is the charge and M_a the mass of the nucleus a . The distances in the denominators of the three potential operators are the absolute values of the vector differences of the respectively indexed particles. Inherent to this ansatz the internal degrees of freedom of the nuclei are not taken into account. But the screening forces of the electrons act at distances far beyond the range of the nuclear forces. The connection to the nucleus takes place via the calculated screening energy U_e in the cross-section. Just as little any spin dependent effects are considered. So polarization effects as observed in [19] cannot be described. Since the impact proceeds at keV-energies the inclusion of relativistic effects is not required. Furthermore, the velocity of the nuclei is small in comparison to the electrons³. Hence, the Born-Oppenheimer approximation [20] can be applied which leads eventually to a drop out of the nuclear operators in (2), leaving (3, 4). The electron wave functions become then continuous functions of the nuclear coordinates. The movement of the projectiles is treated classically owing to the acting forces. The now purely electronic Schrödinger equation can nevertheless only be solved approximately, which is done based on the Ritz theorem by minimization of the energy functional $E[\Psi] = \langle \Psi, \mathbf{H} \Psi \rangle$ with Ψ from a restricted function space \mathcal{F} under control parameters. This is performed with the self-consistent field method by Hartree and Fock (HF). The electronic Hamilton operator is splitted up in a single electron operator (3) and a part containing the interaction potential (4). The single electron problem has likewise solution functions $\varphi(\mathbf{r}, \sigma) := \psi(\mathbf{r}) \chi(\sigma)$ with the space function ψ and the spin function χ . The solution of the multi-electron problem is constructed with the anti-symmetrization operator

as a Slater determinant $\Psi = \mathbf{A} \varphi_a(1) \cdot \varphi_b(2) \cdot \dots \cdot \varphi_n(N)$ in accord with the Pauli principle. The variation of the energy functional yields the Hartree-Fock equations [21]

$$\begin{aligned} \mathbf{H}_{\text{HF}} \psi_a(i) &= -\frac{1}{2} \Delta_i \psi_a(i) - \sum_a^K \frac{Z_a}{r_{ai}} \psi_a(i) \\ &\quad + \sum_b^{n/2} (2\mathbf{J}_b - \mathbf{K}_b) \psi_a(i) \\ &= e_a \psi_a(i) \end{aligned} \quad (5)$$

with the Coulomb operator \mathbf{J}_b and the exchange operator \mathbf{K}_b defined as

$$\begin{aligned} \mathbf{J}_b \psi_a(i) &= \left(\psi_b(j), \frac{1}{r_{ij}} \psi_b(j) \right) \psi_a(i) \\ \mathbf{K}_b \psi_a(i) &= \left(\psi_b(j), \frac{1}{r_{ij}} \psi_a(j) \right) \psi_b(i) \end{aligned} \quad (6)$$

They have the form of an eigenvalue equation for ψ_a with the orbital energy e_a , though they are coupled by the operators \mathbf{J}_b and \mathbf{K}_b . Indeed, they are a system of coupled integro-differential equations which can only be solved iteratively. To simplify matters the case of the restricted HF method is described where all $n/2$ orbitals are occupied with electrons. Otherwise the unrestricted HF method has to be used [22,23]. The HF method furnishes merely a stationary solution so far. A time development can be achieved with the unitary time propagation operator $\psi(t) = \mathbf{U}(t, t_0) \psi(t_0)$ which is given by $\mathbf{U}(t, t_0) = e^{-i(t-t_0)\mathbf{H}}$ if the Hamilton operator is not explicitly time dependent [24]. Caley's form provides a unitary approximation for this equation as a calculable time discretization resulting in the time dependent Hartree Fock method using \mathbf{H}_{HF} [25,26]. Such has been carried out by [27,17] implementing the discretization of the electron wavefunctions on a space lattice.

The HF method cannot include immediate electron-electron interaction⁴. For electrons of equal spin the main correlation effects are incorporated in the Slater determinant. But the motion of electrons of opposite spin remains uncorrelated. To address this, several procedures have been developed which either start from the HF solution functions applying corrections or modify the HF method [23,28,29,30]. They are based on the configuration interaction method (CI) or the Møller-Plesset perturbation theory (MPn). The CI method uses the HF orbital function and adjoins further wherein occupied orbital functions are replaced by unoccupied virtual orbitals successively thus forming a series [22]. The linear coefficients are determined by minimization of the energy functional. This series is infinite and would deliver an exact solution for the Schrödinger equation (3,4) in the limit. In practice, the series is aborted after the first to fourth term with few virtual orbitals in the individual terms. The

² Notations according to [18].

³ The electrons of the inner shells of heavy atoms attain relativistic velocities. This is commonly considered by corrections.

⁴ The operators \mathbf{J}_b and \mathbf{K}_b in (6) merely provide an averaged effective electron potential in the iteration due to the integration in the scalar product, e.g. [18].

MPn method is essentially an implementation of the common quantum mechanical perturbation theory [31]. It is usually aborted after the second to eighth order. Another approach is the density functional theory (DFT) [32,33]. Following the theorem of Hohenberg and Kohn a unique functional exists which provides an exact solution of (3,4) [34,35]. But there is no algorithm that can generate this functional so one needs to settle on heuristic ones and therefore the DFT is no ab-initio method in the end [36, 37, 38, 39, 40, 41, 42]. The DFT modifies the HF equations with an exchange interaction functional, which is to be supplied.

The just described configuration interaction procedures can increase the computational costs by 1 to 3 orders of magnitude relative to the plain HF method [43, chapter 6]. On the other hand the implementation of the orbital functions on space lattices is very cost-intensive and only feasible for few electrons. Hence the analytic HF method of Roothaan and Hall is used for larger systems [44, 45, 46]. There the orbital functions are developed as a linear combination $\psi_a = \sum_n^k c_{na} u_n$ of a set of analytic functions $\{u_n\}_1^k \in L^2(\mathbb{R}^3)$ which are the basis of the finite dimensional product space $\mathcal{F}' = \bigotimes_n^k \mathcal{F}'_n$. Thus the HF equations (5) are transformed to a system of pseudo-linear equations for the linear coefficients which are solved iteratively again. The main computational costs now results from the integrations of the numerous scalar products. The computationally most efficient basis functions for it are the Cartesian Gauß type orbital functions [47]

$$u(\text{GTO}) = x^i y^j z^k e^{-\alpha r^2}, \quad i, j, k \in \mathbb{N}_0 \quad (7)$$

with the sum $l = i + j + k$ yielding the angular momentum quantum number of the orbital. Thereupon basis sets of increasing complexity are constructed being geared to actual atomic orbitals [23]. The computer resource usage scales with the total number of GTO basis functions as $\mathcal{O}(n) \sim n^4$ customarily spanning two orders of magnitude [43, chapter 5]. The common minimal basis set is STO-3G where the atomic orbitals are approached by Slater type orbitals which contain the spherical harmonics and are constructed from 3 GTO's with fixed coefficients, therefore called contracted [48, 49]. Split valence basis sets provide two or more sizes of basis functions for the valence orbitals (e.g. D95 [50], LanL2DZ [51, 52, 53], 3-21G [54, 55, 56], 6-31G [57, 58, 59, 60, 61], 6-311G). Polarized basis sets allow the atomic orbitals to change their shape by providing orbitals with angular momentum higher than for the ground state description, like p and d orbitals (here 6-31G(d,p) [62, 63]). High angular momentum basis sets add more orbitals of p, d, and f type (here 6-311+G(3df,3pd) [64, 65, 66, 67, 68]). The inclusion of diffuse functions adds larger size versions of s and p type functions allowing the orbitals to cover larger regions of space which is advantageous for charge transfers in ionic bonds (indicated by a '+'). Most of the basis sets are only available for the lower periods of the periodic table. Only the LanL2DZ covers heavier atoms where the inner shells are described by effective core potentials including relativistic effects. The extra basis (+XB) adds diffuse functions.

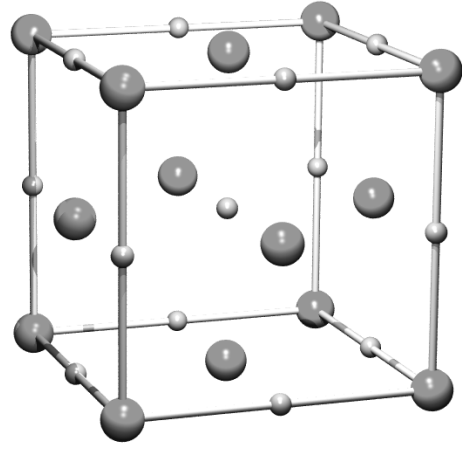


Fig. 1. Cubic space centered crystal cell of LiH.

In consequence, it becomes clear that the simulation of the pre-reaction impact inside the metal lattice involves so many electrons that the task has very high computer resource requirements. For the given workstation (Ultra-SPARC), the problem is actually oversized. So it is un-avoidable to drop the time dependence and settle for the analytic HF method with restricted basis sets and few atoms, possibly augmented by the DFT. The impact is then treated as quasi static. The Coulomb adjusted relative electronic force between the projectile and target nuclei is recorded and integrated along the trajectory T analogous to [27, 17] yielding the molecular screening energy

$$U_{\text{mol}} = \int_T \mathbf{F}_{\text{rel}} \cdot d\mathbf{r} \quad (8)$$

At the classical turning point the molecular screening energy is identified with the screening energy $U_e = -U_{\text{mol}}(r_{cl})$.

So even for stationary orbital functions they are only feasible for relatively small molecules or require super computer scale power.

3 Calculations

The here adopted crystal structure data are taken from [69]. LiH has a cubic space centered structure with $a = 4.085 \text{ \AA}$ [69, III, a1] fig. 1. Ta₂H has a tetragonal structure with $a = 3.38 \text{ \AA}$, $b = 3.41 \text{ \AA}$ [69, IV, j2] fig. 2.

The calculations were performed with different crystalline molecules, basis sets and models for the electron exchange interaction employing the quantum chemical package GAUSSIAN [70]. One such molecule for LiH is depicted in fig. 3. The behaviour of the electrons in this molecule becomes clear by means of the density plots in the intersection through the 4 Li atoms in fig. 4. The total probability density of the electron wavefunction of the molecule is plotted in fig. 4.a. The maximum values are numeralized at the positions of the nuclei. The molecular wavefunction is not normalized to unity but to the number of electrons, i.e. $\int_{\mathbb{R}^3} \Psi^* \Psi d\mathbf{r} = n$. So the probability density values can

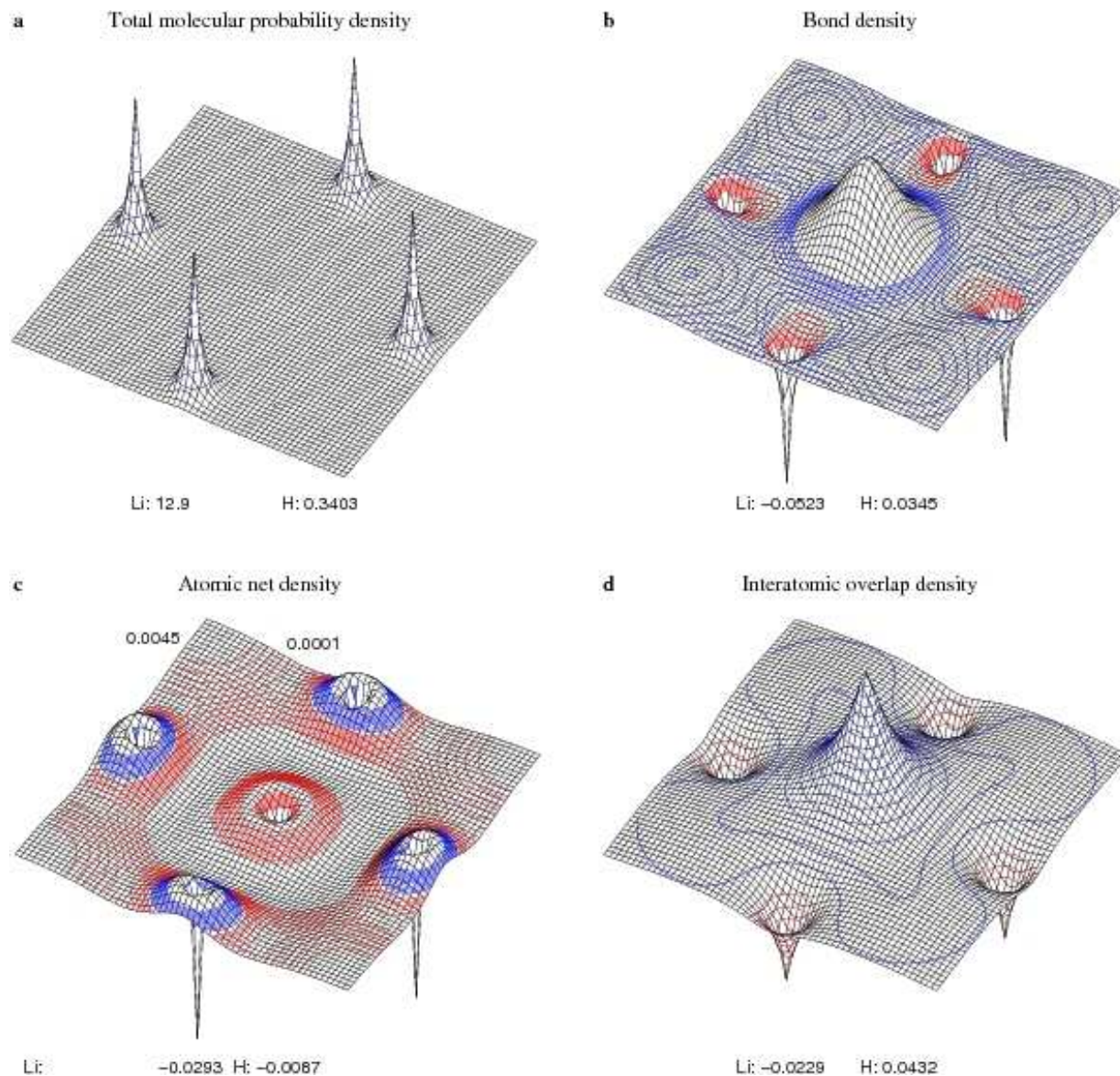


Fig. 4. Different electronic densities in the molecule lih-li1 with the basis 6-31G(d,p)

be larger than 1 and may allow for certain statements on the electron number distribution. The electrons preferentially sojourn at the three fold charged Li nuclei, of course. Hence, the total molecular probability density is not very meaningful in order to observe the shift of the electrons due to the chemical bond. Much more suitable is the bond density (fig. 4.b) which is the difference between the total molecular probability density and the probability density of the single atoms. The result is a plot whose average value is zero and which shows the electron migration when the bonds are formed. Now, it is visible that indeed an electron transfer towards the central hydrogen atom at the expense of the Li atoms took place. The density matrix of the bond density is composed of two parts: the atomic net density (fig. 4.c) which results from setting the interatomic overlap equal to zero. One recognizes where the electrons are deducted from the atoms in order

to form the bonds; from Li in a stronger proportion than from H. The respective maximum values are marked above the plot and the minimum values below. In the overlap density (fig. 4.d) the atomic net density is set to zero and one recognizes the share of the molecular bond. Due to the bond formation the hydrogen atom profits by gaining electron shares. The ionic character of the bond becomes clear, since the overlap at the position of the hydrogen nucleus becomes a maximum and not in between the atoms as in the covalent bond.

The projectile trajectory is chosen so that the projectile does not close in on other nuclei. According to [17] on a nearby passage the spectating nuclei exert a repulsive force on the projectile causing a reduction of the screening energy, on average. On the other hand ions traversing crystal lattices are deflected by the lattice atoms on trajectories inbetween them, known as the channeling effect.

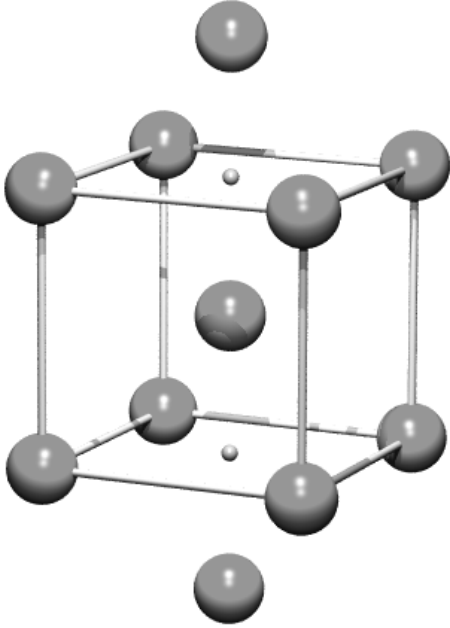


Fig. 2. Tetragonal crystal cell of Ta_2H .

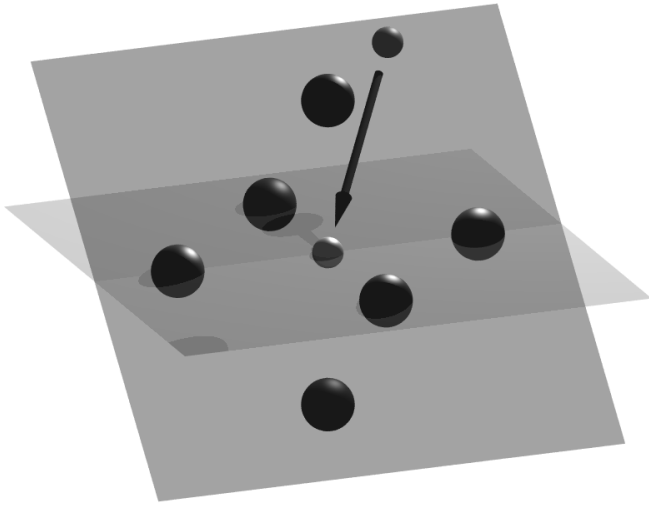


Fig. 3. LiH molecule (lih-li1) with projectile trajectory and intersections.

This means here that the crystal lattice of the metal atoms focuses the incoming deuterons on the interlaced lattice of the deuterons in the metal hydride [71] counteracting the reduction of the screening energy in the D_2 molecule of [17].

During the quasi static simulation of the impact process instant recordings of the bond density at various distances between the projectile and the target were taken which are assorted in fig. 5. The plots of the bond density lie in the intersection of the trajectory of the projectile which is drawn inclined in fig. 3 and contains two Li atoms. For a contrast amplification the bond densities are not rendered with equal scale. At first the bond density is distributed at the projectile and the target. At a distance

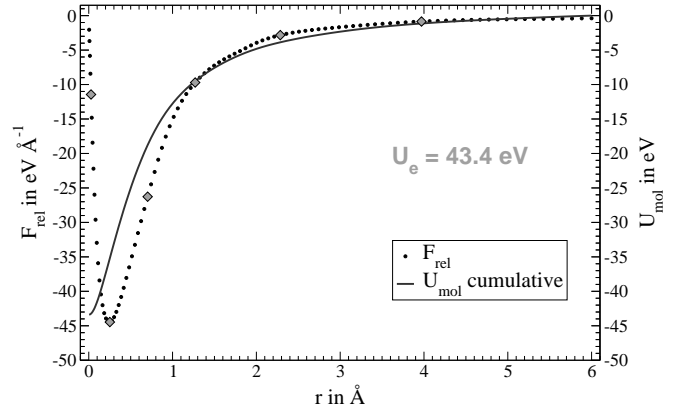


Fig. 6. Relative force and molecular screening energy at the impact in the molecule lih-li1 with the basis 6-31G(d,p).

of 1.269 Å an even enhanced transfer from the target to the projectile and the environment can be observed. From there on the electron transfer from the Li atoms to the hydrogen nuclei approaching each other increases evermore. The calculations were performed for 100 points on the trajectory. The relative forces at these points are plotted in fig. 6. The six points of the bond density plots (fig. 5) are highlighted by rhombuses and mark interesting locations. Beginning at a distance of 6 Å the absolute value of the Coulomb-adjusted relative force raises up to a maximum value at ~ 0.25 Å and declines till zero for further decreasing distances which is understandable because the approaching nuclei virtually form a single one in comparison to the wavelength of the electrons. In so far the behaviour is in accord with the TDHF calculations in [17, fig. 8] except for the oscillations due to the time dependence. The full curve in fig. 6 is the molecular screening energy which was calculated according to (8) along the trajectory at every point. The final result is with -43.39 eV way too low compared to the experimentally obtained values ($\lesssim 150$ eV for Li^5 [16] and $[190, 320]$ eV for the other metals [1, 2, 3]).

The reasons for this unsatisfying result are to be sought in the hierarchy of model assumptions, approximations, and simplifications. Only very few of them could be remedied within the scope of this work. However, some experiments with the bases could be employed whose restrictive impact on the movability of the electrons particularly in the conduction band is of jutting importance. The results of these calculations are summarized in the overview in fig. 7. They are arranged according to increasing complexity of the bases, in each case. Though from the smallest to the largest basis the value of U_{mol} becomes larger only by 10%. Yet the tendency is clear: the larger the basis the higher the screening potential. With an extension of any kind no physical error can be committed since the electrons arrange due to the energy minimization. Only the

⁵ The results for the highly reactive alkaline metals Li and Na are heavily impaired by the surface oxidation under ion irradiation [11].

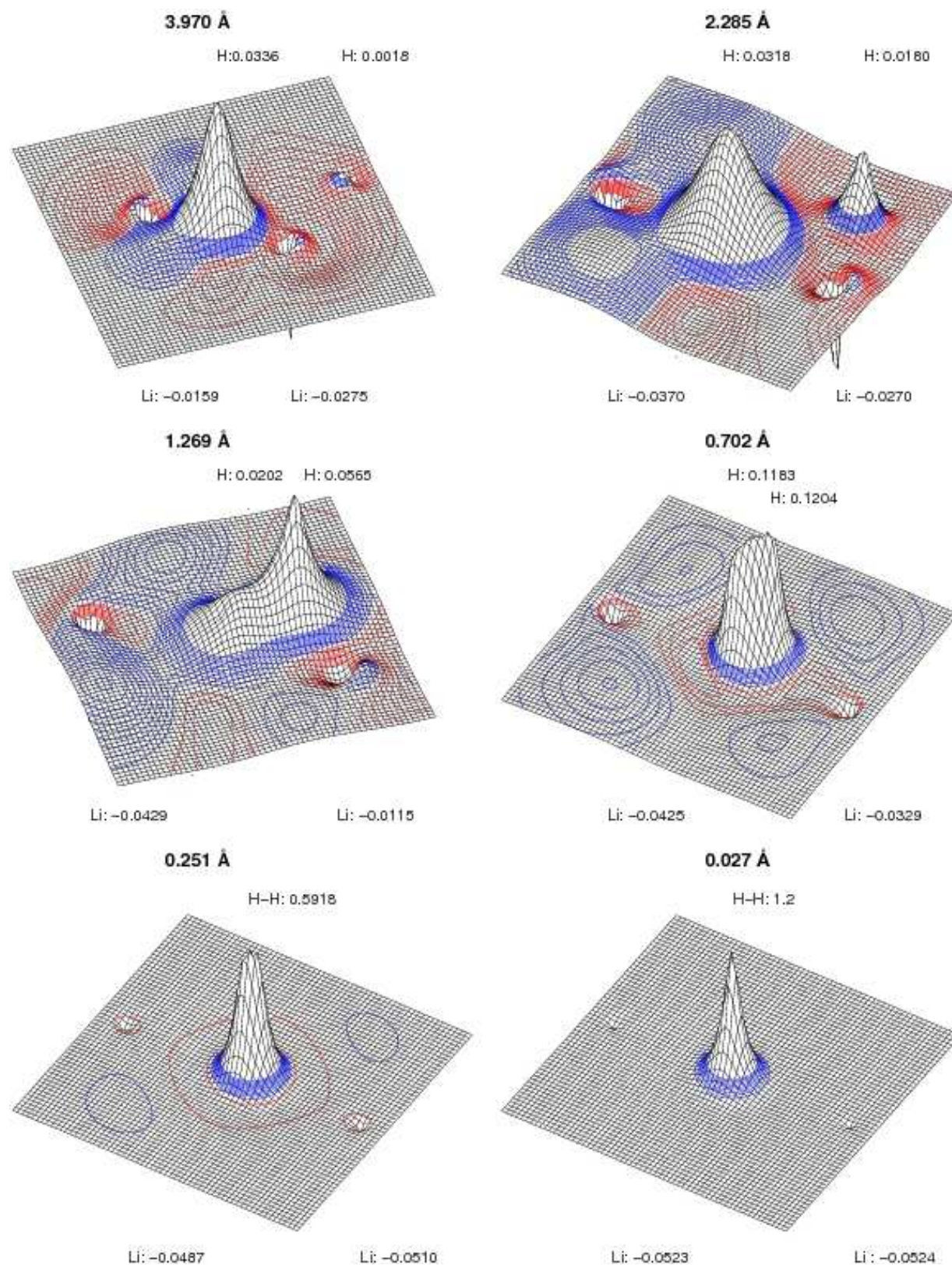


Fig. 5. Instant recordings of the bond density during the impact in the molecule 11h-111 with the basis 6-31G(d,p)

Metal	Molecule	Model	Basis	U_{mol} in eV
Lithium	lih-h2e	HF	LanL2DZ+XB	-40.5337
			6-31G(d,p)	-40.8761
		B3LYP	LanL2DZ	-41.0568
	lih-li1	HF	STO-3G	-41.5753
			LanL2DZ	-42.0125
			LanL2DZ+XB	-43.1172
			6-31G(d,p)	-43.3874
			6-311+G(3df,3pd)	-44.6856
Tantal		HF	LanL2DZ	-39.7167

Fig. 7. Overview of the calculation results.

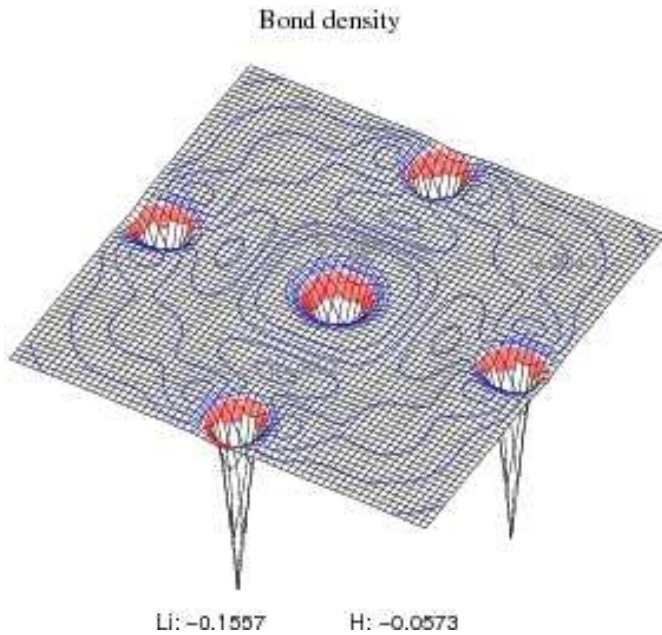


Fig. 8. Bond density in the molecule lih-li1 with the basis STO-3G.

restriction of the bases induces errors. Because the established available bases are centered at the atoms they are hardly suitable for the simplified description of the delocalized electrons of the conduction band.

The effect of the bases on the bond density of the molecule can be assessed by comparison with the smallest basis STO-3G whose bond density is depicted in fig. 8. Unlike the 6-31G(d,p) basis in fig. 4.b no electron transfer to the hydrogen can take place here because the too small basis does not permit enough mobility for the electrons. Instead only between the nuclear positions a weak conglomeration accrues like for the covalent bond.

The impact of the size of the molecule can only be estimated with narrow limitations, since by the addition of further spheres of H and Li atoms around the central target the problem would not be feasible for the worksta-

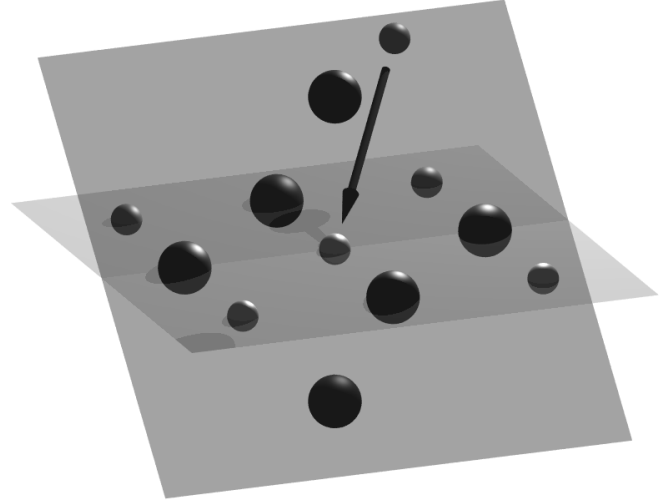


Fig. 9. LiH molecule (lih-h2e).

tion any more. Hence, only on one plane further H atoms were added as fig. 9 shows. The belonging density plots in the plane of the Li atoms (fig. 10) differ perceptibly from those of the simpler molecule (fig. 4). From the comparison of the bond densities, the atomic net and the overlap densities it is apparent that the perimeter H atoms attract electrons on the expense of the central H atom and thus have a higher influx. Accordingly the screening potential is also lower (fig. 7). This behaviour is vitally due to the circumstance that the perimeter H atoms have no Li partners which supply their electrons. If those Li atoms were present the transfer of electrons from the central H atom would be quite perspicuously lower. It is interesting that the maximum values of the bond density form a ring around the central H atom and the maximum values of the perimeter H atoms are not centered around them but shifted towards the central H atom.

Indeed the more complex basis brings higher values for the screening potential here again. Furthermore, it is here also documented how a method affects going beyond the Hartree-Fock method videlicet the density functional theory with the three parameter functional of Becke, B3LYP [38,41,39]. The more accurate provision for the electron correlation effects causes a stronger repulsion of electrons with equal spins and enhances the screening potential. However, this effect is not very large.

A further possibility for a comparison is provided by the Mulliken population analysis which assigns the atoms of the compound a charge according to the electron transfer. Table 1 summarizes those results. The topmost atom is the central target H atom followed by the innermost sphere of metal atoms and further perimeter H atoms. The charges are specified in multiples of the elementary charge. The larger basis for Li provokes an almost ten times higher charge transfer to the H atom compared to the smallest one which yields almost $0.5e$ and underlines the ionic character of the bond. The extended molecule with the four perimeter H atoms permits recognition of the reduction of the charge at the central H atom and the carry-over to the perimeter H atoms. In comparison the

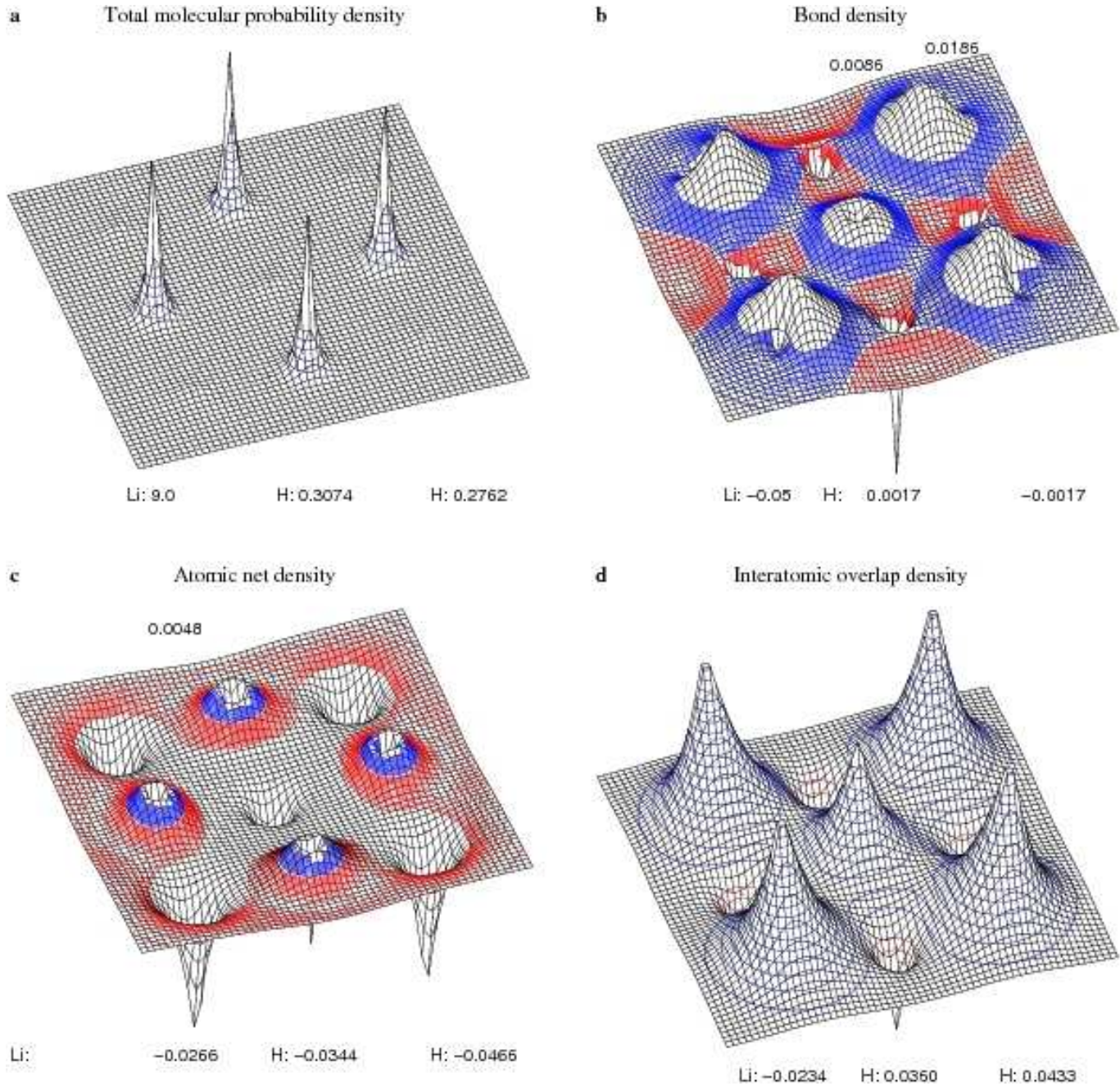


Fig. 10. Different electronic densities in the molecule 1lh-h2e with the basis 6-31G(d,p)

rather high differences in the charge transfers were not reflected to this extent in the differences of the screening potentials (fig. 7). The reason for it is that the charge assignment to the atoms is not a quantum mechanical observable and hence tainted with a certain arbitrariness. This can also be seen at the smallest molecule whose Li atoms are fully symmetrically arranged where two of them donate and four sparsely ingest electrons.

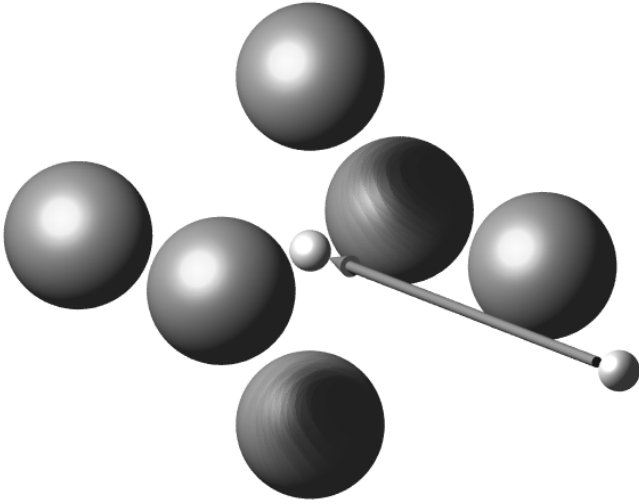
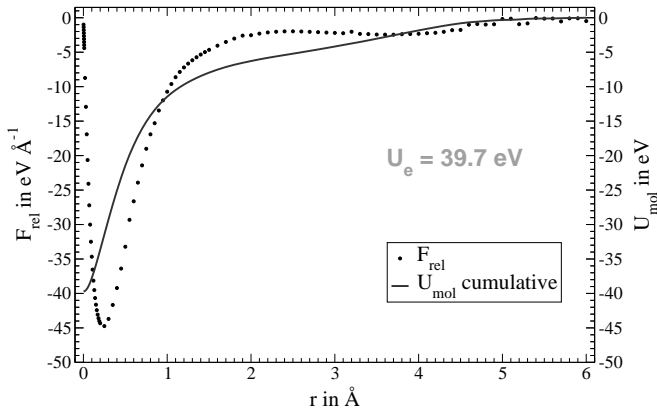
In the right part of the table charge assignments for Tantalum are listed. Owing to the considerable computer time consumption by virtue of the many electrons to be included only one simulation run on the smallest molecule

with the simplest basis could be performed. The result of $U_e = 39.72$ eV even stays behind the smallest Li value, however the charge assignment to the central H atom is not much smaller. The molecule and the projectile trajectory are shown in fig. 11. The behaviour of the relative force in fig. 12 is remarkable. The oscillations in the far field were caused by the large electron clouds with high angular momentum of the Ta atoms.

For details refer to [3].

Table 1. Atomic charges originating from the Mulliken population analysis.

	lih-li1 6-31(d,p)	lih-li1 STO-3G	lih-h2e 6-31(d,p)	LanL2DZ	
H	-0.455479	-0.054858	-0.255553	-0.382043	H
Li	0.336273	0.108454	0.126207	0.030356	Ta
Li	-0.054266	-0.040512	0.126207	0.030355	Ta
Li	-0.054267	-0.040512	0.187523	0.145028	Ta
Li	0.336273	0.108454	0.126207	0.015638	Ta
Li	-0.054266	-0.040512	0.126207	0.145028	Ta
Li	-0.054267	-0.040512	0.187523	0.015637	Ta
H			-0.156081		
H			-0.156081		
H			-0.156081		
H			-0.156081		

**Fig. 11.** Ta_2H molecule with projectile trajectory.**Fig. 12.** Relative force and molecular screening energy at the impact in the molecule Ta_2H .

4 Conclusion

The calculated values for the electron screening energies stay clearly below the experimental ones. The simplifications in the numerical model were enforced by the available computing power. The performed numerical simulations consumed already a netto computation time of 1.6 a. Single points on the trajectory took one week. Anyhow, the simulations could show the migration of electrons from the host metal atoms to the hydrogen both for the target nuclei and the projectile in the impact. This migration becomes larger when the number of base functions is increased. However, in the electron transfer only the immediate adjacent atoms are involved and no distant atoms. This is due to the limited size of the basis which are designed for molecules and not for larger solids. The further extension of the basis sets would provide more freedom of mobility for the electrons. Particularly, the modelling of conduction band states as provided by Bloch wave functions could be an asset. But according to the computational cost function already this extensions to the quasi-static model with an accompanying increase of the crystal size would require the next scale of computational power as computing clusters or super computers. Furthermore, time dependent effects can be expected to contribute the larger share in attaining the experimental screening results particularly when collective interactions between the collision partners and many electrons from a larger region are to be included like plasmons, convoy electrons and effects of the Fermi surface. But a prerequisite for it are a high electron mobility provided by large basis sets. This would require the complete redesign of a computer code for a massive parallel computer worth many man years of work. But then very instructive insights into the electron dynamics for the understanding of the mechanism can be expected which is not accessible in the experiment so far. In exchange for higher code development effort the computational costs could possibly be reduced by three orders of magnitude using the new $\$$ -operator formalism for the solution of partial differential equations by [72].

References

1. K. Czerski, A. Huke, P. Heide, M. Hoeft, and G. Ruprecht. In N. Prantzos and S. Harissopulos, editors, *Nuclei in the Cosmos V*, Proceedings of the International Symposium on Nuclear Astrophysics, page 152, Volos, Greece, July 6-11 1998. Editions Frontières.
2. K. Czerski, A. Huke, A. Biller, P. Heide, M. Hoeft, and G. Ruprecht. *Europhys. Lett.*, 54(4):449–455, 2001.
3. A. Huke. *Die Deuteronen-Fusionsreaktionen in Metallen*. PhD thesis, Technische Universität Berlin, 2002. http://edocs.tu-berlin.de/diss/2002/huke_armin.htm.
4. H. Yuki, J. Kasagi, A. G. Lipson, T. Ohtsuki, T. Baba, T. Noda, B. F. Lyakhov, and N. Asami. *JETP Lett.*, 68(11):823, 1998.
5. J. Kasagi, H. Yuki, T. Baba, T. Noda, T. Ohtsuki, and A. G. Lipson. *J. Phys. Soc. Jpn.*, 71:2281, 2002.
6. F. Raiola et al. *Eur. Phys. J. A*, 13:377, 2002.

7. F. Raiola et al. *Phys. Lett. B*, 547:193, 2002.
8. C. Bonomo et al. *Nucl. Phys. A*, 719:37c, 2003.
9. F. Raiola et al. *Eur. Phys. J. A*, 19:283, 2004.
10. U. Greife, F. Gorris, M. Junker, C. Rolfs, and D. Zahnw. *Z. Phys. A*, 351:107–112, 1995.
11. A. Huke, K. Czerski, and P. Heide. *Nucl. Instr. Meth. B*, 256(2):599–618, 2007.
12. H. J. Assenbaum, K. Langanke, and C. Rolfs. *Z. Phys. A*, 327:461–468, 1987.
13. K. Czerski, A. Huke, P. Heide, and G. Ruprecht. *Europhys. Lett.*, 68(3):363–369, 2004.
14. K. Czerski, A. Huke, P. Heide, and G. Ruprecht. *Eur. Phys. J. A*, 27(S1):83–88, 2006.
15. S. Ichimaru. *Rev. Mod. Phys.*, 65:252, 1993.
16. A. Huke, K. Czerski, G. Ruprecht, N. Targosz, W. Zebrowski, and P. Heide. 2007. submitted.
17. T. D. Shoppa, M. Jeng, S. E. Koonin, K. Langanke, and R. Seki. *Nucl. Phys. A*, 605:387, 1996.
18. Hans-Herbert Schmidtke. *Quantenchemie*. VCH, Weinheim, 2 edition, 1994.
19. A. Huke, K. Czerski, T. Dorsch, A. Biller, P. Heide, and G. Ruprecht. *Eur. Phys. J. A*, 27(S1):187–192, 2006.
20. M. Born and J. R. Oppenheimer. *Ann. der Phys.*, 84:457, 1927.
21. D. R. Hartree. *The calculation of Atomic structures*. John Wiley, New York, 1957.
22. I. N. Levine. *Quantum Chemistry*. Prentice Hall, Englewood Cliffs, 4 edition, 1991.
23. A. Szabo and N. S. Ostlund. *Modern Quantum Chemistry*. McGraw-Hill, New York, 1989.
24. Albert Messiah. *Quantenmechanik*, volume 1. Walter de Gruyter Verlag, Berlin, 2 edition, 1991.
25. A. Goldberg, H. M. Schey, and J. L. Schwartz. *Amer. J. Phys.*, 35:177–186, 1967.
26. I. Galbraith, Y. S. Ching, and E. Abraham. *Amer. J. Phys.*, 52:60–68, 1984.
27. T. D. Shoppa, S. E. Koonin, K. Langanke, and R. Seki. *Phys. Rev. C*, 48:837, 1993.
28. P. Čarský and M. Urban. *Ab initio Calculations*. Number 16 in Lecture Notes in Chemistry. Springer, Berlin, 1980.
29. L. Zülicke. *Quantenchemie*, volume 1. Deutscher Verlag der Wissenschaften, Berlin, 1973.
30. R. J. Bartlett. *J. Phys. Chem.*, 93:1697, 1989.
31. C. Möller and M. S. Plesset. *Phys. Rev.*, 46:618, 1934.
32. R. G. Parr and W. Yang. *Density-Functional Theorie of Atoms and Molecules*. Oxford University Press, 1989.
33. J. K. Labanowski and J. W. Andzelm, editors. *Density Functional Methods in Chemistry*. Springer, Berlin, 1991.
34. P. Hohenberg and W. Kohn. *Phys. Rev. B*, 136:864, 1964.
35. W. Kohn and L. J. Sham. *Phys. Rev. A*, 140:1133, 1965.
36. T. Ziegler. *Chem. Rev.*, 91:651, 1991.
37. S. H. Vosko, L. Wilk, and M. Nusair. *Can. J. Phys.*, 58:1200, 1980.
38. A. D. Becke. *J. Chem. Phys.*, 88:1053, 1988.
39. C. Lee, W. Yang, and R. G. Parr. *Phys. Rev. B*, 37:785, 1988.
40. B. Miehlich, A. Savin, H. Stoll, and H. Preuss. *Chem. Phys. Lett.*, 157:200, 1989.
41. A. D. Becke. *Phys. Rev. A*, 38:3098, 1988.
42. B. G. Johnson, P. M. W. Gill, and J. A. Pople. *J. Chem. Phys.*, 98:5612, 1993.
43. James B. Foresman and Eileen Frisch. *Exploring Chemistry with Electronic Structure Methods*. Gaussian Inc., Pittsburgh, 2 edition, 1996.
44. C. C. J. Roothaan. *Rev. Mod. Phys.*, 23:69, 1951.
45. G. G. Hall. *Proc. Royal Soc. A*, 205:541, 1951.
46. J. P. Pople and R. K. Nesbet. *J. Chem. Phys.*, 22:571, 1954.
47. H. Preuß. *Grundriß der Quantenchemie*. Number 10 in Hochschultaschenbücher. Bibliographisches Institut, Mannheim, 1962.
48. W. J. Hehre, R. F. Stewart, and J. A. Pople. *J. Chem. Phys.*, 51:2657, 1969.
49. J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople. *J. Chem. Phys.*, 64:5142, 1976.
50. T. H. Dunning Jr. and P. J. Hay. In H. F. Schaefer III, editor, *Modern Theoretical Chemistry*, pages 1–28. Plenum Press, New York, 1976.
51. P. J. Hay and W. R. Wadt. *J. Chem. Phys.*, 82:270, 1985.
52. W. R. Wadt and P. J. Hay. *J. Chem. Phys.*, 82:284, 1985.
53. P. J. Hay and W. R. Wadt. *J. Chem. Phys.*, 82:299, 1985.
54. J. S. Binkley, J. A. Pople, and W. J. Hehre. *J. Amer. Chem. Soc.*, 102:939, 1980.
55. M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, and W. J. Hehre. *J. Amer. Chem. Soc.*, 104:2797, 1982.
56. W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. Defrees, J. A. Pople, and J. S. Binkley. *J. Amer. Chem. Soc.*, 104:5039, 1982.
57. R. Ditchfield, W. J. Hehre, and J. A. Pople. *J. Chem. Phys.*, 54:724, 1971.
58. W. J. Hehre, R. Ditchfield, and J. A. Pople. *J. Chem. Phys.*, 56:2257, 1972.
59. P. C. Hariharan and J. A. Pople. *Mol. Phys.*, 27:209, 1974.
60. M. S. Gordon. *Chem. Phys. Lett.*, 76:163, 1980.
61. P. C. Hariharan and J. A. Pople. *Theo. Chim. Acta*, 28:213, 1973.
62. G. A. Petersson, A. Bennet, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley, and J. Mantzaris. *J. Chem. Phys.*, 89:2193, 1988.
63. G. A. Petersson and M. A. Al-Laham. *J. Chem. Phys.*, 94:6091, 1991.
64. A. D. McLean and G. S. Chandler. *J. Chem. Phys.*, 72:5639, 1980.
65. R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople. *J. Chem. Phys.*, 72:650, 1980.
66. A. J. H. Wachters. *J. Chem. Phys.*, 52:1033, 1970.
67. P. J. Hay. *J. Chem. Phys.*, 66:4377, 1977.
68. K. Raghavachari and G. W. Trucks. *J. Chem. Phys.*, 91:1062, 1989.
69. R. W. G. Wyckoff. *Crystal Structures*, volume 1-4. Wiley, New York, 2 edition, 1962-1966.
70. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople. Gaussian 94, revision e.1. Technical report, Gaussian Inc., Pittsburgh, 1995.
71. K. Czerski, A. Huke, P. Heide, and G. Schiwietz. *Nucl. Instr. Meth. B*, 193:183, 2002.

72. Reinhard Starkl. *Neue analytische Methoden der mathematischen Physik*. VWF, Verlag für Wissenschaft und Forschung, Berlin, 1 edition, 1999.